

ON THE  
FLUORINE COMPOUNDS  
OF  
**URANIUM.**

---

INAUGURAL DISSERTATION  
FOR  
THE DEGREE OF DOCTOR OF PHILOSOPHY  
ADDRESSED TO  
THE PHILOSOPHICAL FACULTY  
OF THE  
UNIVERSITY OF GOETTINGEN  
BY  
**H. CARRINGTON BOLTON**  
OF NEW YORK.

---

BERLIN.

PRINTED BY UNGER BROTHERS, PRINTERS TO HIS MAJESTY.

1866.

599.4  
B630  
Chem

P R E F A C E.

The following researches were begun in the Laboratory of the University of Göttingen at the suggestion and under the direction of Professor Wöhler, to whom I here express my heartfelt thanks for the great kindness and unremitting attention conferred upon me during my residence in Göttingen. The investigations were completed in the University Laboratory at Berlin under Professor Hofmann, to whom I also acknowledge my indebtedness.

My sincere thanks are due to Drs. R. Fittig and C. A. Martius the gentlemenly and able assistants in the respective Laboratories, for their kind assistance in this work.

Berlin. January 28th 1866.

14112  
Sub. of Cong. use  
ex.  
23 May 13.  
M. W. K. M.



## N O T E.

Within a very few years the attention of chemists has been directed to the *quantivalence* (or atomicity) of the elements, which has given rise to new theoretical speculations respecting the constitution of chemical bodies. So new are these theories however, that not a few elements remain to which they are still to be applied. Thus it happens that no chemist who has studied *uranium* and its compounds, and none of the literature whether in textbooks, monographs or dictionaries, treats this subject in the light of these modern theories.

In this dissertation therefore the formulae being new, and these necessitating the employment of new names, I have added the old names throughout and occasionally the old formulae; giving to the latter however a subordinate place corresponding to their importance.

Our present knowledge of the uranium compounds is too limited to allow us to establish with any degree of certainty the *quantivalence* of this metal; but the facts warrant the doubling of the old atomic weight as given by Pélégot, and it is taken in the following pages as equal to ( $2 \times 60 =$ ) 120. Should a compound of uranium be hereafter discovered which is sufficiently volatile to admit of determining its vapor-density, and this is by no means improbable, then the true *quantivalence* of the element can be firmly established.



## INTRODUCTION.

In the year 1789, Klaproth<sup>1</sup> discovered in pitchblende a peculiar metallic oxide to which he gave the name uranium. Richter,<sup>2</sup> Bucholz,<sup>3</sup> Lecanu<sup>4</sup> and Brande<sup>5</sup> were among the first to examine this element more closely. In 1823 the literature on uranium was greatly enriched by the labors of Berzelius<sup>6</sup> and Arfvedson,<sup>7</sup> the latter estimating its equivalent which he found equal to 2711 (O = 100). The non-metallic nature of this metal (if the expression may be allowed), its high atomic weight and other discrepancies gave rise to doubts, but it was not until 1840 when Pélégot<sup>8</sup> made known his remarkable discovery that the doubts were confirmed and the discrepancies explained. Pélégot found that the substance till then considered as metallic uranium was in reality an oxide of the true metal and he showed how the latter might be obtained.

Since this date uranium has been a more frequent sub-

---

<sup>1</sup> Beiträge zur chemischen Kenntniss der Mineral-Körper, Vol. II, p. 197.

<sup>2</sup> Neue Gegenstände der Chemie, Vol. I, p. 1. Vol. IX, p. 36.

<sup>3</sup> Gehlen, neues allgemeines Journ. d. Chem., Vol. IV, pp. 17 et 134.

<sup>4</sup> Schweigger's Journ. f. Chem. u. Phys., Vol. XLIV, p. 35.

<sup>5</sup> Schweigger's Journ. f. Chem. u. Phys., Vol. XLIV, p. 1.

<sup>6</sup> Poggend. Annal., Vol. I, p. 359.

<sup>7</sup> Poggend. Annal., Vol. I, p. 245.

<sup>8</sup> Annal. de chim. et de phys., III, Vol. V, p. 5.

ject of research. Rammelsberg,<sup>1</sup> Ebelmen,<sup>2</sup> Wertheim,<sup>3</sup> Kühn,<sup>4</sup> Patera,<sup>5</sup> Drenkmann<sup>6</sup> and others have published their investigations, more or less extensive, on this subject.

It is not my object in this dissertation to give a more complete history of the element uranium, much less to enumerate its various salts, but I will briefly notice its most important compounds with the halogens which stand in close analogy to the fluorine compounds herein discussed. Before entering upon a description of these salts, it will not be out of place to detail the method employed for procuring the nitrate of uranium which forms the starting point in their preparation.

---

<sup>1</sup> Poggend. Annal., Vols LV, LVI et LIX.

<sup>2</sup> Annal. d. Chem. u. Pharm., Vol. XLIII, p. 286.

<sup>3</sup> Journ. f. prakt. Chemie, Vol. XXIX, p. 209.

<sup>4</sup> Annal. d. Chem. u. Pharm., Vol. XLI, p. 337.

<sup>5</sup> Journ. f. prakt. Chemie, Vol. LXI, p. 397; Chem. Centralbl. 1856 etc.

<sup>6</sup> Zeitschr. f. d. gesammten Naturw., Vol. XVII, p. 113. Jahresber. 1861, p. 255.



## EXTRACTION OF URANIUM FROM PITCHBLENDE.

The only mineral which occurs in sufficient abundance to be employed as a source of uranium is the well known pitchblende (uranpecherz). I received through the kindness of Prof. Wöhler a quantity of pitchblende from Joachimsthal in Bohemia. It was of a brownish black color with a dull metallic lustre and remarkably free from gangue. The finely pulverized mineral was digested in a porcelain vessel with concentrated sulphuric and nitric acids until the greater portion was dissolved; the excess of sulphuric acid was then expelled by heat.

The mass was treated with water and the filtrate from the white residue was heated and saturated with sulphuretted hydrogen. After standing twenty four hours it was filtered, the iron and uranium in solution were oxidized with chlorate of potassium and hydrochloric acid while boiling, and then thrown down by an excess of ammonia. This mixed precipitate was well washed and digested with a strong hot solution of carbonate of ammonium until the precipitate assumed the appearance of oxide of iron. The hot solution of uranium was then quickly filtered and yellow crystals of the double salt carbonate of uranium and ammonium  $(UO)_2 CO_3 + 2 (NH_4)_2 CO_3$  deposited on cooling. The mother liquid united to the wash-water (which was collected separately) yielded by boiling a precipitate of

hydrated oxide of uranium,  $U_2O_3 \cdot H_2O$ . By calcining these two salts and dissolving the green oxide formed in nitric acid, large crystals of nitrate of uranium  $(UO)NO_3$  were obtained which were purified by recrystallization.\*

Advantage was taken of the comparatively large scale of operations to submit the several residues to a careful qualitative analysis and with the following results. The first white insoluble portion was found to consist chiefly of sulphate of lead, with small quantities of bismuth and lime. The precipitate by sulphuretted hydrogen contained arsenic, copper, bismuth, a trace of selenium and a not inconsiderable quantity of silver. Whether the latter formed a constituent of the pitchblende, or whether its presence should be attributed to the fact that the mineral came from the neighborhood of silver mines, I could not determine. The filtrate from the mixed precipitate of iron and uranium contained manganese and magnesia. On treating the green oxide with nitric acid, it was not completely dissolved. The yellowish residue was melted with carbonate of sodium, dissolved in hot water, and after filtering from the uranate of sodium which formed, the solution gave with chloride of ammonium the reaction characteristic of vanadium.

To recapitulate: the pitchblende from Joachimsthal contained arsenic, selenium, lead, copper, bismuth, silver, uranium, iron, manganese, a trace of vanadium, magnesia-lime and silicic acid.

---

\* Wöhler's „Mineral Analyse in Beispielen“ p. 156 et seq.

## I. URANIUM AND CHLORINE.

BICHLORIDE OF URANIUM,  $\text{UCl}_2$ , (protochloride of uranium,  $\text{UCl}$ ) discovered by Pélégot forms the material for the preparation of the metal. It is prepared by heating a mixture of the protoxide or of the green oxide with charcoal in a tube through which a current of dry chlorine is passing. It is a dark green volatile body crystallizing in octahedra and exceedingly deliquescent in a moist atmosphere. Its solution is decomposed by evaporation with disengagement of hydrochloric acid. When heated with sodium or potassium it yields metallic uranium in small globules; but notwithstanding the violence of the reaction the heat developed is not sufficient to fuse the metal, and it can be obtained only in very small quantities.

A SUBCHLORIDE has been obtained by heating the bichloride in a current of hydrogen, which according to Rammelsberg has the formula  $\text{U}_2\text{Cl}$ ,  $\text{UCl}$  but according to Pélégot  $\text{U}_2\text{Cl}$ ,  $2\text{UCl}$ . It dissolves in water with a purple color, but quickly decomposes with disengagement of hydrogen and precipitation of a reddish powder, the hydrate of the protoxide; the solution at the same time turning green.

OXICHLORIDE OF URANIUM,  $(\text{U}\Theta)\text{Cl}$ , (old notation  $2\text{U}_2\text{O}_3$ ,  $\text{U}_2\text{Cl}_3$ ) may be obtained by heating the protoxide,  $\text{U}\Theta$ , in a current of dry chlorine; as thus prepared it is a crystalline, fusible, slightly volatile body, soluble in water, alcohol and ether. Crystals of the same may be procured by evaporating the yellow solution obtained by dissolving the sesquioxide of uranium  $\text{U}_2\Theta_3$  in hydrochloric acid. When heated with potassium this salt yields chloride of

potassium and protoxide of uranium. This compound forms a series of double salts with the chlorides of the alkaline metals, as follows:

OXICHLORIDE OF URANIUM AND CHLORIDE OF POTASSIUM,  $(U\Theta)Cl + KCl + H_2\Theta$  (old notation,  $U_2 O_2 Cl, KCl + 2 aq.$ )

This salt is prepared by dissolving uranate of potassium in hydrochloric acid and crystallizing the solution over sulphuric acid. The beautiful large greenish yellow rhombic plates form best in an acid solution and do not admit of recrystallization. When heated in a closed tube, it melts, parts with its water of crystallization and undergoes partial decomposition. If heated in a current of hydrogen it is decomposed with evolution of hydrochloric acid and leaves a greenish opaque residue.

OXICHLORIDE OF URANIUM AND CHLORIDE OF SODIUM, as well as the corresponding salt of AMMONIUM, have been prepared, but crystallize with great difficulty being deliquescent.

## II. URANIUM AND BROMINE.

BIBROMIDE OF URANIUM,  $UBr_2$  (Protobromide of uranium  $UBr$ ) was first prepared by Hermann.\* It is obtained by heating protoxide of uranium in a current of dry bromine gas, and constitutes a brownish crystalline mass which emits fumes in the air and deliquesces.

HYDRATED BIBROMIDE OF URANIUM,  $UBr_2 + 4H_2\Theta$  (Hydrated protobromide of uranium,  $UBr + 4HO$ ). Rammelsberg obtained this salt by dissolving the hydrate of the

---

\* Inaug. Dissertat. Göttingen 1861.

protoxide in hydrobromic acid and evaporating the green solution in a desiccator.

OXIBROMIDE OF URANIUM,  $(U\Theta)Br$  (old notation,  $2U_2O_3 \cdot U_2Br_3$ ) has been prepared by dissolving the hydrated sesquioxide in hydrobromic acid. It crystallizes in yellow deliquescent needles. Whether crystallized double salts can be obtained with the bromides of the alkaline metals has not been examined.

### III. URANIUM AND IODINE.

The only compound of uranium and iodine as yet prepared is a BI-IODIDE  $UI_2$  (protoiodide  $UI$ ), containing water and obtained by Rammelsberg in treating the hydrated protoxide with hydriodic acid. Its properties have not been completely described.

### IV. URANIUM AND CYANOGEN.

No compound of uranium and cyanogen has been yet procured.

### V. URANIUM AND FLUORINE.

(HISTORICAL.)

The fluorine compounds of uranium have been very little studied. The first notice of a compound of uranium and fluorine is made by Berzelius in his "Researches on Hydrofluoric Acid and its most remarkable Compounds" which appeared in the first volume of Poggendorf's *Annalen* in 1824.\* He briefly describes the oxifluoride of

---

\* The original reads: "Untersuchungen über die Flussspathsäure und deren merkwürdigsten Verbindungen".

uranium as soluble in water and forming a yellow uncrystallizable solution. Later (1845) in his "Lehrbuch der Chemie" he repeats the facts before stated, gives the formula  $U_2Fl_3 + 2U_2O_3$  and adds that the solution yields with the fluorides of the alkaline metals yellow crystallizable double salts. Berzelius also describes the silicofluoride of uranium as a bluish green precipitate and mentions further that the "protofluoride" (bifluoride) is unknown.

No chemist appears to have more closely examined these compounds until 1861 when Hans Hermann published his dissertation "On some Compounds of Uranium", in which he examined the action of hydrofluoric acid on the proto-sesquioxide of uranium and describes the "protofluoride" (bifluoride) as a "sesquifluoride" having the formula  $U_2Fl_3$ .

He gives the method of preparation and of analysis (though unfortunately no figures) and adds that this "sesquifluoride" contains water which is only expelled by a temperature of  $200^\circ C$ . I trust however it will be satisfactorily demonstrated in the following pages that the substance in question is an anhydrous bifluoride.

## BIFLUORIDE OF URANIUM. $\text{UFl}_2$

(PROTOFLUORIDE OF URANIUM.  $\text{UFl}$ .)

PREPARATION I. Hydrofluoric acid in solution acts upon the green oxide of uranium with considerable vigor, causing an appreciable elevation of temperature; a yellow solution is formed together with an insoluble green powder which latter is the object of our immediate attention. If the acid employed be somewhat concentrated, the yellow solution is sirupy and admits of filtration, but it is nearly impossible to wash the precipitate upon the filter for it possesses the property of passing through the pores of the paper even if double or fourfold filters are employed. Long continued boiling of the solution with the precipitate does not prevent its persistently running through the filter. By operating upon comparatively large quantities, sufficient of the bifluoride was collected for examination and analysis; but it was far from being pure, and hence the figures given in the analyses of the salt as thus prepared are inaccurate.

PROPERTIES. The bluish green powder is insoluble in water and scarcely attacked by dilute acids; even concentrated nitric acid dissolves it but slowly. When boiled with a solution of caustic soda, it is decomposed and insoluble black protoxide of uranium is formed which is dehydrated by continued heating. The solution contains fluoride of sodium. If heated strongly on platinum foil it is decomposed with loss of fluorine and formation of the green oxide, without melting. When heated in a closed tube

it is found to contain no water. The green powder being in an exceedingly fine state of division is hygroscopic.

ANALYSIS. The salt having been dried at  $100^{\circ}$  C. a weighed quantity was dissolved by the aid of heat in concentrated nitric acid. The solution was diluted, the uranium precipitated with a slight excess of ammonia and this precipitate was washed partly by decantation partly on the filter with a dilute solution of chloride of ammonium. The uranate of ammonium was dried and ignited (with the filter) in a platinum crucible and weighed as  $\text{U}\Theta \text{U}_2\Theta_3$ .

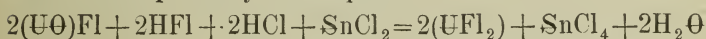
I.	0.8553	gram.	substance	gave	0.7368	gram.	$\text{U}_3\Theta_4 = 73.1\%$	U
II.	1.1845	"	"	"	1.0310	"	"	= 73.8 " U
III.	0.8270	"	"	"	0.7197	"	"	= 73.8 " U
	0.8270	"	"	"	0.3820	"	$\text{CaFl}_2 = 22.5$	" Fl
	The formula		$\text{U}_2\text{Fl}_6$		requires		67.7	% U
	"	"	$(\text{U}\Theta)\text{Fl}_2$		"		68.9	" "
	"	"	$\text{UFl}_2 + \text{H}_2\Theta$		"		68.1	" "
but	"	"	$\text{UFl}_2$		"		75.9	" " and
							24.1	" Fl.

Therefore although the figures are far from satisfactory a glance shows the formula  $\text{UFl}_2$  to be without doubt the true one.

PREPARATION II. Bifluoride of uranium may be obtained in a state of purity by reducing the oxifluoride of uranium by means of bichloride of tin. For this purpose the yellow solution resulting from the action of hydrofluoric acid on the green oxide of uranium, is heated in a platinum vessel with bichloride of tin as long as the green bifluoride falls. If hydrofluoric acid is added from time to time during the reduction, the whole of the uranium is precipitated and the filtrate is colorless, containing only the per-salt of tin.



Instead of the solution of the oxifluoride obtained as above mentioned, a solution of uranate of ammonium (or even of the double salt of carbonate of uranium and ammonium) in hydrofluoric acid may be employed with equal advantage. The following equation shows the reaction which most probably takes place:



As thus prepared the precipitate may be washed upon a filter without the least difficulty, and its behavior with reagents proves its identity with the salt obtained by the preceding method.

ANALYSIS. The uranium was estimated in this salt precisely as in the previous analysis. The fluorine was determined in a separate portion as follows: a weighed quantity of the salt dried at  $100^\circ \text{C}$ . was boiled with a strong solution of caustic potassa until the green color entirely disappeared, and the black protoxide of uranium was collected on a filter and washed with boiling water. This precipitate was weighed but found to contain potassa.

The filtrate was *nearly* neutralized with acetic acid and the fluorine thrown down by chloride of calcium. Carbonate of potassium in excess being present (the potassa having absorbed carbonic acid from the air, its addition is superfluous) carbonate of calcium falls with the fluoride of calcium, which is absolutely necessary to prevent the latter passing through the filter. The mixed precipitate was dried and ignited with the filter. The carbonate of calcium was dissolved out with acetic acid, the excess of acid driven off by evaporating nearly to dryness on a water-bath, and the fluoride of calcium was then brought upon a filter and washed until the filtrate no longer gave a

precipitate with oxalic acid. The precipitate was again ignited and weighed. The following are the results obtained.

- I. 0.7920 grm. substance gave 0.3910  $\text{CaFl}_2 = 24.0\%$  Fl  
 II. 0.7778 grm. " " 0.6936  $\text{U}_3\text{O}_4 = 75.5\%$  U  
 III. 0.7200 grm. " " 0.6484  $\text{U}_3\text{O}_4 = 76.4\%$  U

The formula  $\text{UFl}_2$  requires the following percentage:

Calculated.		Found.		
		I.	II.	III.
U	= 120.    75.9	....	75.5	76.4
$\text{Fl}_2$	= $\frac{38.}{158.}$ $\frac{24.1}{100.0}$	24.0	....	....

PREPARATION III. Hydrofluoric acid acts upon the protoxide of uranium very slowly and yields bifluoride of uranium.\* As thus prepared it has the property of passing through filtering paper. No analysis of it was made.

PREPARATION IV. Hydrofluoric acid converts freshly precipitated hydrated protoxide of uranium into the bifluoride immediately. The green precipitate formed also possesses the property of passing through filters. I did not consider an analysis of this necessary.

PREPARATION V. Hydrofluoric acid produces in a solution of the bichloride of uranium  $\text{UCl}_2$  a green gelatinous precipitate which is so voluminous that a moderately concentrated solution of the uranium salt solidifies. On adding water and agitating the precipitate it settles; and when washed by decantation or upon the filter retains its gelatinous form. By drying this precipitate however over sul-

---

\* Hans Hermann, in his dissertation already referred to, mentions this reaction but maintains the formation of a "sesquifluoride" which is impossible.

phuric acid *in vacuo* or at  $100^{\circ}$  C. it diminishes greatly in volume and yields a greenish powder a shade lighter than when prepared by any of the previous methods. Two estimations of the uranium made in the manner already described gave the following results.

1.0308 grm. of the salt dried at  $100^{\circ}$  C. gave 0.8725 grm. of the proto-sesquioxide, which is equal to 71.8 per cent U; and 0.4460 grm. of the same gave 0.3795 grm. of the green oxide or 72.1 per cent U.

The formula  $\text{UFl}_2$  requires 75.9 per cent uranium but the formula  $2(\text{UFl}_2) + \text{H}_2\text{O}$  requires 71.8 per cent uranium, and it would appear that this is a hydrate which only imperfectly loses its water at  $100^{\circ}$  C.

The water estimations made gave however no satisfactory results, and the further examination of this salt was abandoned.

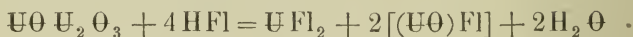
A SUBFLUORIDE (?) was obtained by heating the bifluoride in a current of dry hydrogen. Hydrofluoric acid was given off and a reddish brown powder formed on the surface; by pulverizing the aggregated mass, heating again in hydrogen and repeating the operation several times, the greater portion assumed a reddish color.

This substance is quite insoluble in water and scarcely attacked by acids, concentrated nitric acid excepted. It was not further examined but probably corresponds in composition to the *subchloride* obtained under similar conditions.

## OXIFLUORIDE OF URANIUM.

(U $\theta$ )Fl.

(Old notation,  $U_2Fl_3 + 2U_2O_3$ ). Hydrofluoric acid only partially dissolves the green oxide of uranium; the green bifluoride remaining insoluble may be collected on a filter though as before mentioned the latter cannot be washed out. The yellow solution shows the same reactions as that which Berzelius\* obtained by dissolving hydrated sesquioxide of uranium in hydrofluoric acid and is evidently identical with it. Accepting the composition of this body given by Berzelius, viz, (U $\theta$ )Fl its formation is expressed in the following equation:

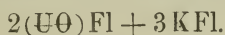


No analysis of this salt was made but a few of its properties were examined. The yellow solution is uncrystallizable, and on evaporation yields a nearly white mass which dissolves again in water without decomposing. It is also soluble in alcohol, and on evaporating this solution it furnishes a yellow, transparent, amorphous mass which is very deliquescent. This salt retains water when dried at 100° C. If heated in a closed tube it is only partially decomposed, the residue being somewhat soluble in hydrochloric acid. When heated on platinum foil, it loses fluorine and the green oxide of uranium remains. Finally, when the solution of the salt is heated with tin and hydrochloric acid, the green bifluoride of uranium is precipitated as already mentioned.

---

\* Poggend. Ann. Vol. I, p. 34.

## OXIFLUORIDE OF URANIUM AND FLUORIDE OF POTASSIUM.



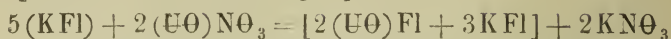
PREPARATION I. Fluoride of potassium added to a solution of the nitrate of uranium produces a heavy crystalline precipitate of a lemon yellow color. This precipitate being but sparingly soluble, may be washed upon a filter with cold water to free it from an excess of fluoride of potassium and from the nitrate of potassium which forms; and being more abundantly soluble in hot water it may be purified by dissolving in hot water and allowing the solution to crystallize, either from the hot concentrated solution or by evaporation of the cold solution over sulphuric acid.

In preparing this salt it is of advantage to use a slight excess of fluoride of potassium,\* the salt being soluble in nitrate of uranium. According to the analysis made, the details of which are given below, this salt was found to

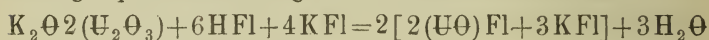
\* The fluoride of potassium employed must be free from silico-fluoride of potassium, hence the following precautions observed in its preparation.

Selected crystals of pure fluor spath (as free from quartz as possible) were finely pulverized in an iron mortar and gently heated with concentrated sulphuric acid in a platinum retort. The hydrofluoric acid was absorbed by distilled water contained in a platinum capsule and after the distillation ceased, the acid solution was neutralized with pure carbonate of potassium. If notwithstanding these precautions a small quantity of silico-fluoride of potassium forms, it may be separated by filtering through platinum or gutta-percha funnels.

contain  $2(\text{U}\Theta)\text{Fl} + 3\text{KFl}$ ; its formation may be therefore expressed in the following equation:



PREPARATION II. The oxifluoride of uranium and potassium may also be procured by dissolving freshly precipitated uranate of potassium in hydrofluoric acid, adding fluoride of potassium and crystallizing. The necessity of adding fluoride of potassium is made evident by the following equation\* showing the formation of the salt:



PREPARATION III. The same salt may be procured by adding fluoride of potassium to a solution of the hydrated oxide of uranium in hydrofluoric acid, or to the oxifluoride of uranium as obtained by the action of hydrofluoric acid on the green oxide of uranium. These methods however possess no advantages over the foregoing.

In the hope of preparing the salt in question in the dry way, I made the following experiment. A small quantity of the double salt sulphate of uranium and potassium was prepared by heating the nitrate of uranium with concentrated sulphuric acid and neutralizing with potassa. This double salt was finely pulverized, intimately mixed with fluoride of sodium and some previously dried sulphate of sodium (as a flux), the mixture introduced into a Hessian crucible which was maintained at a red heat for more than an hour and then allowed to cool in the furnace. The result however was unsatisfactory; the greater part of the sulphate of uranium and potassium remained unchanged, with the exception of the formation of a small amount of uranate of sodium near the surface of the melted mass.

PROPERTIES. The oxifluoride of uranium and potassium crystallizes in small yellow plates. I obtained crystals grouped in three different ways: *first*, by the cooling of a hot concentrated solution, a crust of minute crystals formed upon which rested larger individual prisms; *secondly*, by the *spontaneous* evaporation of a cold solution well defined twin crystals formed, easily distinguishable without a magnifying glass though not more than two millimeters in diameter; *thirdly*, I accidentally obtained a number of warty concretions consisting of concentric rings of small crystals and completely spherical. They formed at a low temperature. The crystals thus obtained are small but often well formed and possess a high lustre but not the brilliant *fluorescence* peculiar to the corresponding oxichloride. Containing no chemically combined water they do not effloresce.

I am indebted to Prof. Victor von Lang, who had the kindness to measure crystals of this salt, for the following data.

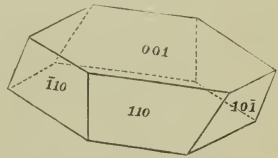
Crystalline system: Monoclinic.

$$a : b : c = 1.375 : 1 : 3.477$$

$$a c' = 99^{\circ} 40'$$

Observed forms = (001), (110), ( $\bar{1}01$ ). Fig. 1.

	Calculated	Observed
$001 \cdot \bar{1}01 = 77^{\circ} 0'$	$77^{\circ} 0'$	$77^{\circ} 0'$
$001 \cdot 110 = 82^{\circ} 14'$	$82^{\circ} 14'$	$82^{\circ} 14'$
$110 \cdot \bar{1}10 = 72^{\circ} 50'$	$72^{\circ} 50'$	$72^{\circ} 50'$
$110 \cdot 10\bar{1} = 56^{\circ} 47'$	$58^{\circ}$	



The crystals as seen in fig. 1 are plates, the planes (001) predominating.

The twin crystals of the same salt furnished the following.  
Crystalline system: Tetragonal.

$$a : c = 1 : 2.0815$$

Observed forms: (101), (104), (001).

Fig. 2.

	Calculated	Observed
$101 \cdot 001$	$= 64^\circ 20'$	$64^\circ 20'$
$101 \cdot 10\bar{1}$	$= 51^\circ 20'$	$51^\circ 20'$
$104 \cdot 001$	$= 27^\circ 29'$	
$101 \cdot 104$	$= 36^\circ 51'$	$36^\circ 50'$
$101 \cdot 011$	$= 79^\circ 11'$	$78^\circ 30'$
$102 \cdot 001$	$= 46^\circ 8'$	



The crystals are penetration twins formed on a plane (102), both individuals equally developed. The planes (104), (001) occur rarely. Optical character negative.

When heated in a closed tube, the salt *melts*, forming a red liquid which solidifies and resumes its yellow color on cooling; it undergoes partial decomposition. If heated on platinum foil with free access of air it melts as before and loses its fluorine, an infusible mass remaining which has a deep crimson color while hot and turns orange-yellow on cooling. This yellow residue on examination proved to be uranate of potassium.

The salt does not decompose in boiling water; it is of neutral composition, but shares the property of other neutral uranium salts of reddening slightly blue litmus. The salt in solution does not attack glass even when concentrated and boiling; hence glass vessels may be employed in examining the salt though platinum ones are necessary in its preparation. The salt is insoluble in alcohol and ether, the former precipitating it finely divided from the aqueous solution. An estimation of the solubility of the salt was made by evaporating a weighed amount of a concentrated solution and after drying the residue at  $100^\circ \text{C}$  weighing the crucible and contents a second time.



Thus, 8.6812 grms of the concentrated solution at 21° C yielded on evaporation 0.9653 grm. of the salt. By calculation, therefore, 100 parts of water at 21° C dissolve 12.5 parts of the salt.

The salt is decomposed by melting with carbonate of sodium, forming uranate and fluoride of sodium. The action of reagents on the solution of the salt is as follows: *ammonia* produces the usual precipitate of uranate of ammonium; the *carbonates of sodium and ammonium* do not decompose the salt on boiling; *chloride of barium* gives even in dilute solutions a voluminous white precipitate which settles in the form of a crystalline powder; this change is accelerated by heating; *acetate of lead* gives an orange yellow precipitate very soluble in dilute acids, the filtrate still contains uranium; *chloride of calcium* gives a white transparent precipitate from which it is impossible to filter; solutions of *silver, copper, iron, mercury, platinum and zinc* are without action; *oxalic or formic acids* and the *direct rays of the sun* produce a green precipitate.\*

By heating the salt in a current of hydrogen gas, hydrofluoric acid is disengaged and the greenish residue consists of a mixture of bifluoride of uranium, *protoxide of uranium* and fluoride of potassium. This experiment demonstrates most clearly the presence of oxygen.

QUANTITATIVE ANALYSIS. (a) The crystallized salt having been dried over sulphuric acid, a weighed portion was heated in a platinum crucible with concentrated sulphuric acid and when the fluorine was completely expelled the excess of acid evaporated. The temperature was gra-

---

\* See page 33.

dually raised until the crucible was at a low red heat, its contents melting without projections. After dissolving out the contents of the crucible, ammonia was added to throw down the uranium and this precipitate treated as usual. Since uranate of ammonium precipitated in presence of the fixed alkalies has a tendency to combine with them, the green oxide of uranium after having been weighed was dissolved in nitric acid and reprecipitated by ammonia, washed, ignited and weighed as before. The second weighing showed a loss of twelve tenths of a milligramme (0.0012 grm.) which is too inconsiderable to affect the analysis and is to be attributed to inaccuracy of manipulation rather than to the presence of potassa in the first precipitate.

(b) The filtrate was evaporated to dryness in a platinum dish on a water-bath, the residue gently calcined until all chloride and sulphate of ammonium were expelled and the remaining sulphate of potassium was dissolved in a few drops of water filtered into a platinum crucible, again evaporated, ignited and weighed. Since it is necessary to wash the uranate of ammonium with a dilute solution of chloride of ammonium, the estimation of the potassium as just detailed is exceedingly tedious.

(c) The determination of the fluorine presented many difficulties. The precipitate of fluoride of calcium obtained by adding chloride of calcium to the solution of the potassium salt is in an extremely fine state of division and runs through the filter notwithstanding every precaution. The estimation of the fluorine as fluoride of lead was not deemed sufficiently accurate or available in this case, and the following method was pursued which though imperfect gave such results as warranted its use. A weighed quantity

of the salt was melted with three to four times its weight of carbonate of sodium in a platinum crucible; the melted mass after being cooled was treated with water which dissolved out the fluoride of sodium and the excess of carbonate of sodium leaving *crystallized* uranate of sodium for the most part undissolved. The fluorine was then thrown down in the filtered solution by chloride of calcium and the mixed precipitate of carbonate and fluoride of calcium treated exactly as described in the analysis of bifluoride of uranium.

In the two estimations made the fluoride of calcium was colored yellow owing to the partial solubility of uranate of sodium in carbonate of sodium.

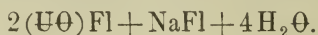
The results obtained are as follows:

I.	0.9453	gram.	substance	gave	0.5542	gram.	$U_3\Theta_4 = 49.8\%$	$U$
	"	"	"	"	0.5040	"	$K_2SO_4 = 23.9\%$	$K$
II.	0.6316	"	"	"	0.2450	"	$CaFl_2 = 18.9\%$	$Fl$
III.	0.6810	"	"	"	0.2680	"	$CaFl_2 = 19.12\%$	$Fl$

These numbers correspond to the formula  $2(U\Theta)Fl + 3KF$  as follows:

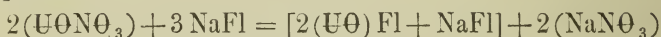
Calculated.		Found.		
		I.	II.	III.
$U_2 = 240.$	49.59	49.86	....	....
$\Theta_2 = 32.$	6.62	....	....	....
$Fl_5 = 95.$	19.61	....	18.90	19.12
$K_3 = 117.$	24.18	23.90	....	....
	<u>484.</u>			
	100.00			

**OXIFLUORIDE OF URANIUM  
AND  
FLUORIDE OF SODIUM.**

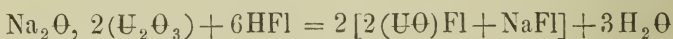


I. This salt though more difficult to procure than the foregoing, crystallizes far better if one succeeds in employing the proper proportions of its constituents.

By evaporating a mixture of nitrate of uranium and fluoride of sodium in a desiccator, I obtained monoclinic prisms of considerable size and great beauty, but many trials subsequently made were unsuccessful in reproducing them. The analysis having given the above constitution of the double salt, its formation may be expressed by the equation:



A solution of uranate of sodium in hydrofluoric acid when slowly evaporated over sulphuric acid furnishes similar crystals, but neither in this case could I find the conditions requisite for their certain formation. This method should theoretically be more advantageous than the previous one in which nitrate of sodium forms and interferes with the crystallization but it did not prove as successful. The reaction is as follows:



PROPERTIES. This salt is by no means so stable as the corresponding potassium salt; it decomposes on attempting to recrystallize it, or if its solution is heated, fluoride of sodium crystallizing out separately.

Prof. Victor von Lang who also measured these crystals has furnished the following data.

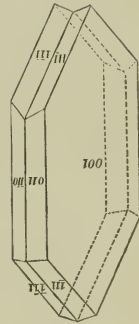
Crystalline system: monoclinic.

$$a : b : c = 1.0272 : 1 : 0.5222. \quad a c = 94^{\circ} 51'$$

Observed forms: (100), (110), ( $\bar{1}11$ ), ( $\bar{1}32$ )

Calculated	Observed
$110 \cdot 100 = 45^{\circ} 40'$	$45^{\circ} 40'$
$\bar{1}11 \cdot \bar{1}00 = 69^{\circ} 20'$	$69^{\circ} 20'$
$\bar{1}11 \cdot \bar{1}\bar{1}1 = 51^{\circ} 20'$	$51^{\circ} 20'$
$\bar{1}11 \cdot \bar{1}10 = 56^{\circ} 11'$	$55^{\circ}$
$\bar{1}32 \cdot 100 = 97^{\circ} 41'$	$98^{\circ}$
$\bar{1}32 \cdot \bar{1}10 = 58^{\circ} 19'$	$60^{\circ}$

Fig. 3.



The crystals are juxtaposition twins on the plane (100) and as seen in fig. 3 appear as thin plates by the predominance of the same plane.

When heated in a closed tube, it gives off its water of crystallization, and on raising the temperature melts, the residue consisting of uranate of sodium. In a dry atmosphere it effloresces. Its properties in general resemble those of the potassium salt, and the analysis was simply a repetition of that described at length in the preceding section.

When the crystallized salt is heated at  $100^{\circ}$  C. it loses two atoms of water = 8.4 per cent.

I. 1.2230 grms. cryst. salt gave 0.8205  $U_3\Theta_4 = 56.9\%$  U  
 1.2230 " " " " 0.2340  $Na_2SO_4 = 6.2\%$  Na

The formula  $2(U\Theta)Fl + NaFl + 4H_2O$  requires the following percentage:

	Calculated.	Found.
$U_2 = 240,$	56.6	56.9
$\Theta_2 = 32,$	7.54	....
$Fl_3 = 57,$	13.44	....
$Na = 23,$	5.42	6.2
$4H_2\Theta = 72,$	17.0	....
	<hr/> 424	<hr/> 100.00

II. On endeavoring to recrystallize this salt it partially decomposes, and other smaller crystals form containing two atoms less of water. This salt is not efflorescent.

The analysis gave the following results:

I. 1.0755 grms. cryst. salt gave 0.7765 gm.  $\text{U}_3\text{O}_4 = 61.3\% \text{U}$

II. 0.8699 " " " " 0.2730 gm.  $\text{CaFl}_2 = 15.1\% \text{Fl}$

These figures correspond to the formula  $2(\text{U}\Theta)\text{Fl} + \text{NaFl} + 2\text{H}_2\Theta$  as follows:

	Calculated.	Found.
$\text{U}_2 = 240,$	61.85	61.3
$\Theta_2 = 32,$	8.24	....
$\text{Fl}_3 = 57,$	14.69	15.1
$\text{Na} = 23,$	5.92	....
$2\text{H}_2\Theta = 36,$	9.30	....
	<hr/> 388,	<hr/> 100.00

## OXIFLUORIDE OF URANIUM AND FLUORIDE OF AMMONIUM.



By dissolving uranate of ammonium in hydrofluoric acid and evaporating the solution over sulphuric acid, but few distinct crystals were obtained. On account of the difficulty of preparing this salt in a pure state no quantitative analysis of it was made, but only a few of its properties examined.

This yellowish imperfectly crystallized mass is very soluble in water, less soluble in a solution of hydrofluoric acid and quite insoluble in alcohol. When heated on platinum foil it is completely decomposed the green oxide

remaining. When heated in a closed tube, water is at first given off, fluoride of ammonium sublimes and condenses on the sides of the tube. The residue in this case is also the proto-sesquioxide of uranium.

This salt has most probably a composition corresponding to the foregoing salts of potassium and sodium, which may be expressed in general terms as follows:  $x(\text{U}\Theta)\text{Fl} + y\text{RFl} + z\text{H}_2\Theta$ . "R" being the alkali metal.

## OXIFLUORIDE OF URANIUM AND FLUORIDE OF BARIUM.



**PREPARATION.** The addition of chloride of barium to a solution of the oxifluoride of uranium and potassium produces a voluminous lemon yellow precipitate which gradually settles in the form of a crystalline powder. This precipitate being quite insoluble in cold water may be washed on the filter until free from chloride of barium and when dried at  $100^\circ \text{C}$ . forms a yellowish white powder which under a powerful microscope resolves into minute crystals. If, in preparing this salt, the oxifluoride of uranium and potassium is not perfectly free from fluoride of potassium, the insoluble uranium salt will be mixed with fluoride of barium which being equally insoluble cannot be separated.

**PROPERTIES.** Hot water dissolves only a trace of this salt, but it is quite soluble in dilute acids. This acid solution yields a white precipitate of sulphate of barium with sulphuric acid, and the filtrate a yellow precipitate

of uranate of ammonium with ammonia. On heating the salt in a closed tube, water is disengaged, and at a higher temperature hydrofluoric acid. The salt does not melt during the decomposition.

ANALYSIS. The quantitative analysis was conducted as follows; a given quantity was dissolved in dilute hydrochloric acid, and the solution being heated to boiling, the barium was thrown down with a slight excess of sulphuric acid. The uranium was precipitated by ammonia and estimated as  $U_3O_4$ . The fluorine was estimated in the filtrate in the same manner as in the analysis of the preceding salts. The salt dried at  $100^\circ C$ . still retains water which was estimated according to a method proposed and employed by Berzelius and recommended by H. Rose.\* A weighed quantity of the salt was introduced into a porcelain crucible and well mixed with four to five times its weight of previously calcined litharge. The crucible was weighed first empty then with the salt and then after the addition of the oxide of lead; the covered crucible was cautiously brought to a low red heat and after cooling in the desiccator was weighed again. The difference in weight before and after calcining is due to the water driven off, the fluorine being retained by the lead.

Result of the analyses:

I.	0.7222	gram.	substance	gave	0.4178	$BaSO_4$	=	33.9	%	Ba
	"	"	"	"	0.3564	$U_3O_4$	=	41.8	"	U
II.	0.6427	"	"	"	0.3720	$BaSO_4$	=	35.3	"	Ba
	"	"	"	"	0.3140	$U_3O_4$	=	41.1	"	U
	"	"	"	"	0.2110	$CaF_2$	=	15.9	"	Fl
III.	0.5538	"	"	"	0.0192	$H_2O$	=	3.4	"	$H_2O$

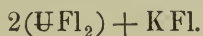
\* Chimie Analytique. Vol. II, p. 758.



The formula  $4(\text{U}\Theta)\text{Fl} + 3\text{BaFl}_2 + 2\text{H}_2\Theta$  corresponds to the figures obtained as follows:

Calculated.			Found.		
			I.	II.	III.
$\text{U}_4$	= 480,	40.6	41.8	41.1	....
$\Theta_4$	= 64,	5.4	....	....	....
$\text{Fl}_{10}$	= 190,	16.1	....	15.9	....
$\text{Ba}_3$	= 411,	34.8	33.9	35.3	....
$2\text{H}_2\Theta$	= <u>36,</u>	<u>3.1</u>	....	....	3.4
	1181.	100.0			

## FLUORIDE OF URANIUM AND POTASSIUM.



PREPARATION. Formic acid produces no precipitate in the solution of the oxifluoride of uranium and potassium, but if the acidified solution is placed in the direct rays of the sun decomposition begins almost immediately; a green precipitate gradually falls, and if the action is prolonged, the solution becomes colorless and retains only a trace of uranium.

The precipitate washed upon a filter and dried at  $100^\circ \text{C}$  forms a green impalpable powder much resembling the bifluoride of uranium. This reaction appears to be best effected in dilute solutions.

PROPERTIES. This double fluoride is quite insoluble in water and in dilute acids. It dissolves with difficulty in concentrated boiling hydrochloric acid, but is more easily decomposed with concentrated sulphuric acid which expels the fluorine and yields a green solution. Ammonia produces in this solution a black precipitate of hydrated

protoxide of uranium and the filtrate on evaporation yields sulphate of potassium.

When heated on platinum foil the salt melts, hydrofluoric acid is disengaged and the yellow residue consists of uranate of potassium. This reaction distinguishes this double salt in a marked manner from the bifluoride. When heated in a closed tube, i. e. without access of air, the decomposition is different. The salt melts and gives off hydrofluoric acid as before, but the residue consists of black protoxide of uranium suspended in fused fluoride of potassium. If heated with a solution of caustic soda, it is decomposed with formation of the black protoxide, while the fluorine goes into solution. When heated in a current of dry hydrogen, it melts, hydrofluoric escapes and the same reddish powder is formed which was obtained by treating the bifluoride of uranium in a similar manner. On cooling the mass was found to be green within, the surface only having been attacked. No further examination of this was made.

ANALYSIS. The analysis of this salt was made in exactly the same manner as that of the oxifluoride, only remarking that the solution in sulphuric acid was oxidized with fuming nitric acid before throwing down the uranium with ammonia. The potassium was estimated in the ordinary way as sulphate.

The following figures show the results of the analysis.  
 0.7535 grm substance gave 0.5640 grm  $U_3O_4 = 63.4\% U$   
 " " " " 0.1852 "  $K_2SO_4 = 11.0\% K$

The formula  $2(UFl_2) + KFl$  requires the following percentage:

	Calculated.	Found.
U <sub>2</sub> = 240.	64.1	63.4
Fl <sub>5</sub> = 95.	25.5	....
K = 39.	10.4	11.0
	<u>374.</u>	<u>100.0</u>

## QUANTITATIVE REDUCTION OF THE OXIFLUORIDE OF URANIUM AND POTASSIUM.

As already remarked the reducing action of formic acid in the sunlight is very complete so that only a trace of uranium remains in solution, and the resulting salt being quite insoluble I conceived the idea of effecting the reaction *quantitatively*, and as the figures below indicate, succeeded beyond expectation.

The method of making this *quantitative analysis by means of the sunlight* needs no lengthy description. A quantity of the potassium double salt was dried at 100° C, weighed, dissolved in water acidified with formic acid and the solution exposed to the direct rays of the sun during two (short winter) days. So long a time was necessary for although decomposition begins at once and is at first rapid it gradually decreases in intensity as the solution becomes weak. The green precipitate was collected on a filter previously dried at 100° C and weighed and after being washed with cold water, the filter and contents were dried at 100° C and weighed as before. Thus two weighings sufficed to give data for calculating the formula of the salt and at the same time to confirm the formula adopted for the oxifluoride.

1.0635 grm. oxifluoride gave 0.8205 grm. of the precipitate.

$$\begin{array}{ccccccc} \text{Weight of salt} & & \text{is to} & \text{its equivalent} & \text{as} & \text{weight of} & \text{is to its equivalent} \\ \text{employed} & & & & & \text{precipitate} & \\ 1.0635 & : & & 484 & = & 0.8205 & : & x \\ & & & & & & & x = 373.6 \end{array}$$

The formula  $2(\text{UFl}_2) + \text{KFl}$  has the equivalent = 374.0

A second analysis was made in like manner. 1.1530 grm. of the oxifluoride gave 0.8783 grm. of the precipitate. In place of stating the proportion as above it may also be put thus:

$$\begin{array}{ccccccc} \text{Equiv. of} & & \text{is to} & \text{equiv. of double} & \text{as} & \text{weight of} & \text{is to} & \text{weight of} \\ \text{oxifluoride} & & & \text{fluoride} & & \text{oxifluoride} & & \text{precipitate} \\ 484. & : & & 374. & = & 1.1530 & : & x \\ & & & & & & & x = 0.8888 \text{ grm.} \end{array}$$

whereas the weight actually received = 0.8783 grm.

## REDUCTION OF THE OXIFLUORIDE OF URANIUM AND POTASSIUM BY MEANS OF OXALIC ACID AND SUNLIGHT.

Oxalic acid with the aid of sunlight decomposes the oxifluoride of uranium and potassium in much the same manner as formic acid, but with the formation of secondary products. The green insoluble fluoride of uranium and potassium falls as before, but after the decomposition has reached a certain stage, a brownish red precipitate also forms.

This proved to be hydrated protoxide of uranium, discovered by Ebelmen\* and obtained by him through the

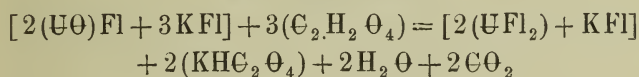
---

\* Annal. d. Chem. u. Pharm. Vol. XLIII.

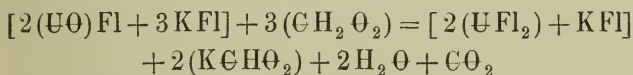
action of the sun's rays on a solution of the oxalate of uranium. This hydrate however being soluble in dilute acids is easily separated from the quite insoluble fluoride.

During the decomposition by oxalic acid a considerable quantity of carbonic acid disengages; of course carbonic acid must be also set free when the decomposition is effected with formic acid, but only half as much is theoretically formed and this is probably absorbed by the water for in no case did I observe its escape. The following equations giving the action of these two acids are probably not absolutely correct but only approximatively so, since Ebelmen mentions the formation of carbonic oxide as well as of carbonic acid.

With oxalic acid:



With formic acid:



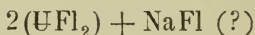
An experiment made with the object of effecting the reduction at a high temperature without the aid of sunlight, was unsuccessful. A solution of the oxifluoride acidified with formic acid was heated in a sealed tube at 100° C. and afterwards at 120° C. but without producing the least change.

In a sealed tube which stood for several weeks in diffuse daylight a small quantity of the green precipitate formed, the glass being at the same time somewhat attacked by the fluorine. On opening the tube carbonic acid gas escaped from the solution.

The oxichloride of uranium and potassium corresponding

to the fluorine salt and having the formula  $(UO)Cl + KCl + 2aq$  could not be reduced by means of formic or oxalic acids in the sunlight; nor by heating an acidified solution in a sealed tube at  $120^{\circ} C$ .

## FLUORIDE OF URANIUM AND SODIUM.



When a solution of the oxifluoride of uranium and sodium is acidified with formic or oxalic acids and exposed to the direct rays of the sun, a reduction takes place in much the same manner as in the case of the potassium salt. The properties too of the precipitate differ little from those of the corresponding potassium compound, but it appears to be somewhat soluble in water since the solution becomes green and not colorless after a lengthened exposure. Neither does it melt when heated on platinum foil but simply loses fluorine and leaves uranate of sodium characterized by its yellow color. I made no analysis of this salt, but it probably possesses the composition given in the above formula.

---

As much as the application of Pélignot's uranyle theory simplifies the formulae of many compounds of uranium they become still more simple when combined with the modern double atomic weights and the unitary system of notation. The following table of a few of the most important salts of uranium gives in the first column the old names and formulae and in the second the new.

Uranium	U = 60	Uranium	U = 120
Protoxide	UO	Protoxide	U $\Theta$
Sesquioxide	U <sub>2</sub> O <sub>3</sub>	Sesquioxide	U <sub>2</sub> U <sub>3</sub>
Sulphide	US	Sulphide	U $\S$
Oxisulphide	U <sub>2</sub> O <sub>2</sub> S	Sulphide of uranyle	(U $\Theta$ ) <sub>2</sub> S
Protochloride	UCl	Bichloride	UCl <sub>2</sub>
Oxichloride	U <sub>2</sub> Cl <sub>3</sub> + 2U <sub>2</sub> O <sub>3</sub>	Chloride of uranyle	(U $\Theta$ )Cl
Oxichloride of uranium and chloride of potassium	KCl + U <sub>2</sub> O <sub>2</sub> Cl + 23q	Chloride of uranyle and potassium	KCl + (U $\Theta$ )Cl + H <sub>2</sub> U
Protofluoride	UF <sub>3</sub>	Bifluoride	UF <sub>2</sub>
Oxifluoride	U <sub>2</sub> F <sub>3</sub> + 2U <sub>2</sub> O <sub>3</sub>	Fluoride of uranyle	(U $\Theta$ )F
Oxifluoride of uranium and fluoride of potassium	2(U <sub>2</sub> O <sub>2</sub> F) + 3KF <sub>3</sub>	Fluoride of uranyle and potassium	2(U $\Theta$ )F + 3KF <sub>3</sub>
Oxifluoride of uranium and fluoride of sodium	2(U <sub>2</sub> O <sub>2</sub> F) + NaF + 8HO	Fluoride of uranyle and sodium	2(U $\Theta$ )F + NaF + 4H <sub>2</sub> U
Sulphate of protoxide	UOSO <sub>3</sub>	Sulphate of uranium	U $\S$ O <sub>4</sub>
Sulphate of sesquioxide	U <sub>2</sub> O <sub>3</sub> SO <sub>3</sub>	Sulphate of uranyle	(U $\Theta$ ) $\S$ O
Nitrate of sesquioxide	U <sub>2</sub> O <sub>3</sub> NO <sub>5</sub>	Nitrate of uranyle	(U $\Theta$ )N $\Theta$ <sub>3</sub>
			etc.



3 0112 072830224

On comparing the chlorine with the fluorine compounds (the bromides and iodides being as yet too little studied) the most marked difference is the greater *stability* of the latter. While the bichloride of uranium is volatile, very soluble and even deliquescent, the corresponding fluoride is not in the least volatile and is quite insoluble in water.

The double salts of potassium too show the same distinctive character. The chloride of uranyle and potassium is obtained with greater difficulty and cannot be recrystallized, while the fluorine salt forms easily and crystallizes repeatedly from its solutions.

It is certainly remarkable that while the fluorine salt exhibits such a sensibility to the sun's rays (in presence of a reducing agent) the chlorine salt does not possess this in the smallest degree. Might not this double fluorine salt be employed to estimate the power of the sun's actinic rays? For as we have seen, the green precipitate which forms only in the sunshine is so insoluble as to admit of effecting the reaction quantitatively.